Mobile Lab Quality Improvement Plan Implementation

August 9, 2016

On June 21, GAI issued a draft Mobile Lab Quality Improvement Plan that proposed several Action Items to be taken for evaluation of Pace mobile lab QA/QC procedures and reliability of onsite inline process monitoring sample results. The tables below describe the steps taken to implement each of Action Items identified in the Mobile Lab Quality Improvement Plan. Further efforts to improve mobile lab performance will be determined based on on-going evaluations of inline process monitoring and compliance sample results.

Analytical Uncertainty Action Items

GAI Action Item	Execution Summary
• GAI performed a Level 2 review of the mobile lab's QA/QC procedures. The results of this review will be incorporated into an overall onsite lab data QA/QC evaluation. Moving forward, Level 2 reviews of the mobile lab's QA/QC procedures will be conducted on a weekly basis. Analytical method improvements resulting from the Level 2 data review will be implemented by the week of 6/19/2016.	• Weekly Level 2 reviews of mobile lab QA/QC lab results have been implemented. • Pace has added a note to their draft reports to help address drift in continuing calibration.
• GAI is working on improvements to the mobile lab environmental conditions. Improvement options being considered include relocating all GAI staff to the Glover/GAI trailer, installation of a partition between the analytical portion of the lab and the office area where GAI staff is located, removing the wall between the Machine A and Machine B, improvement of the existing air conditioning system, installation of heat sinks below the lab floor, development of regular maintenance and cleaning procedures, and improvement of existing electrical/power infrastructure. Selected improvements will be implemented on the week of 6/19/2016 and 6/26/2016.	• Pace has installed larger AC units to equilibrate temperature. • Access to the lab by samplers has been minimized to reduce the tracking of dirt/dust into the lab and to help maintain a cooler temperature. • The second entrance to the lab trailer has been closed off, leaving one entrance/exit pathway for GAI and Pace employees to reduce the tracking of dirt/dust into the lab and to help maintain a cooler temperature. • Pace was initially directed to remove the wall between the two analytical machines to equilibrate temperature. It was determined that the removal of the wall would produce a significant amount of dust and debris, potentially interfering with instrument performance. As a result, this change will not be implemented. • An extra Pace lab technician is now scheduled during the M-F day shifts to assist with cleaning and maintenance activities. This was initiated after the holiday break for the Fourth of July. • GAI received a recommendation from the manufacturer of the window AC units to forgo installation of HEPA filters in order to avoid potential issues due to freezing. • A new chiller has been installed for Machine B. • A quote for a Clean Room for the Pace Mobile Lab has been received. Use of a Clean Room will provide further improvement of environmental conditions within the mobile lab space. However, this Clean Room may not be able to be implemented for this project because of argon storage concerns.
• GAI requested that calibration of the ICP-MS instruments in the mobile lab be performed every 12 hours, increasing the calibration frequency from its original schedule of once every 24 hours. This will implemented on the week of 6/19.	• Pace has prepared and implemented an optimal operation and calibration schedule based on a 12 hour cycle for when both Instruments are functional. Please see Attachment D (Pace Memorandum) for more details.
• GAI collected split samples to be analyzed by a third party offsite lab (AWS) and the onsite lab for comparison. Samples collected on 6/20, 6/21, 6/23, 6/24, and 6/25 will be used to evaluate the impact of the different analytical methods (digestion vs. non-digestion) as well as the impact of sample turbidity on analytical results.	• The Split Sample Analysis as proposed has been completed. Linear regressions were prepared to compare corresponding data sets. A copy of the Split Sample Analysis and the resulting conclusions has been included as Attachment A to this document. • Turbidity measurements were not collected concurrently with collection of split samples. Ongoing monitoring of influent turbidity and internal process samples will be used to assess the impact of turbidity.

Analytical Uncertainty Action Items (Continued)

GAI Action Item	Execution Summary
• GAI collected split samples for analysis by each of the two ICP-MS instruments onsite (Machines A and B). We will review the QA/QC data provided by Pace for each machine to identify potential reasons for differences between measurements produced by the two instruments. This review will be completed by the week of 6/19/2016. •	• A comparison of split sample results (6/22/16) from Machines A and B showed differences between measured concentrations of arsenic, selenium, thallium, and zinc (see Table 1 below). Observed differences between arsenic, thallium, and zinc concentrations were within the range of tolerance provided by the instruments. • According to Pace, the observed differences in measured selenium concentrations are likely the result of inconsistent ambient temperatures in the lab trailer. As the temperature of the Machine rises from the temperature during calibration, recovery of selenium at lower concentrations begins to fall. This is more prevalent with Machine A, so Pace has recommended using this machine during the night shifts to reduce selenium drift occurrences. Pace has also installed additional AC in the mobile lab trailer to address this issue. • GAI has developed a spreadsheet to perform trend analyses using inline process monitoring split sample data split samples by each of the two ICP-MS instruments onsite (Machines A and B). This trend analysis will be maintained as the project progresses and as additional split samples are obtained. GAI has prepared an analysis comparing split sample results from Machines A and B, and the resulting conclusions have been included as Attachment C to this document. • Pace will add a LCV check using a selenium standard of 5 ppb following every sample batch submission to increase reliability of results. Using a 5 ppb standard will provide more useful information of how the system is operating at/near the "target limit" and the increased frequency will make it easier to follow and detect any analyte drift that is occurring on the instrument being used. Please see Attachment D (Pace Memorandum) for more details.
• GAI will perform an on-site audit/technical review of the mobile laboratory, including a review of their collection procedures (SOPs), client sample procedures, test procedures, CER compliance, and GAI QA/QC procedures. Checklists for the audit will be completed by the week of 6/26/2016. It is anticipated that the audit will be performed during the week of 7/3, and results will be available the week of 7/10.	• A technical review was completed by GAI on 6/29 – 6/30. The review included completion of technical review checklists for the following items: onsite mobile lab; compliance sampling; CER compliance; VPDES permit compliance; SWPPP compliance; and O&M Manual compliance. Pace's SOP was updated to address these findings in Rev. 2 which was implemented on 7/12. • An additional QA/QC review of site operations was performed by GAI on 7/11 – 7/12. The findings of this review are being addressed in the Rev. 3 of the SOP. This revision should be implemented in early August and will be used going forward. • GAI conducted an informal QA/QC assessment of site operations during the week of 7/25. As a result Pace developed recommended an optimal operation and calibration schedule for the Instruments and additional LCV checks using a selenium standard of 5 ppb. This is detailed above and in Attachment D (Pace Memorandum). These changes will also be captured in Rev. 3 of the SOP.
• GAI is performing a comparison of split samples collected by Glover and shipped to TestAmerica for analysis and samples collected and analyzed by the onsite mobile lab. This review will be completed by the week of 6/19/2016.	• Results for three split samples were evaluated (see Table 2 below). All constituents demonstrated comparable results, with the exception of selenium. Observed selenium concentrations were very close to one another, and inline process sample selenium measurements were higher than TestAmerica measurements in each of the three samples. The difference between onsite lab and TestAmerica lab results for selenium ranged from 0.7 – 1.3 ppb.
• GAI will perform a trend analysis using compliance and inline process monitoring sample data. This trend analysis will be performed continuously and will be used to identify deviations in data.	• GAI has developed a spreadsheet to perform trend analyses using inline process monitoring and compliance sample data. This trend analysis will be maintained as the project progresses and as additional split samples are obtained. • GAI has prepared an analysis comparing the Compliance sample data with Internal Process sampling results for each Compliance sample that has been collected to date (18 events). Selenium, thallium and zinc were the only parameters where there were any results with a quantifiable difference between Compliance and Internal Process sampling data. A copy of this analysis and the resulting conclusions has been included as Attachment B to this document.

Sample Variability Action Items

GAI Action Item	Execution Summary
• In response to the observed differences between the compliance and inline process monitoring sample results from 6/13, GAI revised Table 8 of the O&M Manual to include more stringent limits on all metals. It is anticipated that this revised table will be modified again once the discrepancies between the two sets of lab data have been resolved.	• GAI has continued to use the revised version of Table 8 as laboratory QA/QC issues are addressed. The Column C concentration for selenium was increased to 6.8 ppb based on approval by Dominion. The acceptability of this limit has been verified by split sample comparisons of onsite mobile lab and offsite digested lab sample data (see Attachment A).
• GAI is performing an inventory of the pipeline from the lake tanks to the compliance sampling trailer to locate potential zinc/metal contamination sources. This will be completed by the week of 6/19/2016.	• An inventory of the pipeline was completed on 6/22, and a summary of the findings was submitted internally on 6/23. This review identified brass fittings in several locations, including hose barbs and valves in the compliance sampling trailer. All observed brass fittings have been replaced with stainless steel fittings as of 7/29/2016 within the compliance sampling trailer.
• GAI will analyze the compliance samples collected on 6/13 and 6/15 using the onsite mobile lab instruments. The results of this analysis will provide a more direct comparison between the results produced at the onsite mobile lab and at the offsite compliance lab. This analysis is expected to be completed the week of 6/19/2016.	• Results from reanalysis of the compliance samples collected on 6/13 and 6/15 are shown in Tables 3 and 4 below, respectively. An observable difference was noted for thallium measurements. • GAI has evaluated this difference further with additional split samples between the mobile lab and offsite labs. Split samples collected on 6/20, 6/21, 6/23, 6/24, and 6/25 did not contain enough thallium measurements above the limit of detection to provide sufficient data for a linear regression analysis. The results of these additional split samples are detailed in Attachment A. Additional split sample data will be collected as the project progresses, and the difference between thallium measurements from the onsite and offsite lab will be evaluated as more data becomes available.

Turbidity & pH Action Items

GAI Action Item	Execution Summary
• GAI has requested that Sequoia/ProAct begin monitoring turbidity at the sample collection port and at the treatment system influent. If elevated levels of turbidity (> 1 NTU) are observed consistently, GAI will request that ProAct implement improvements to the treatment system for reduction of turbidity.	• Daily turbidity monitoring of the Lake Tank effluent began on 6/23. To date, all effluent turbidity measurements have been < 1.0 NTU.
• GAI is evaluating the pH of the 6/13/16 sample vs. other compliance samples taken to date. This will be completed by the week of 6/19/2016.	• The observed pH of the 6/13/16 sample was 6.65. Previous compliance sample measurements have ranged from 6.99 – 7.75. The impact of decreased pH on analytical results will continue to be evaluated. Currently, not enough data is available to draw any conclusions regarding the impact of pH on analytical results.

Table 1 – Onsite Process Monitoring Lab Split Sample Comparison (Machine A vs. Machine B) – 6/22/2016

Constituent	Machine A	Machine B	Machine A	Machine B
	160622-1049-AET (A)	160622-1049-AET (B)	160622-1132-AET (A)	160622-1132-AET (B)
Antimony (ug/L)	3.2	3.4	3.3	3.2
Arsenic (ug/L)	1.6	1.4	1.7	1.4
Cadmium (ug/L)	< 0.040	< 0.040	< 0.040	< 0.040
Chromium (ug/L)	< 0.86	< 0.86	< 0.86	< 0.86
Copper (ug/L)	< 0.56	< 0.56	< 0.56	< 0.56
Lead (ug/L)	< 0.21	< 0.21	< 0.21	< 0.21
Mercury (ug/L)	< 0.048	< 0.048	< 0.048	< 0.048
Nickel (ug/L)	2.0	1.8	2.0	1.9
Selenium (ug/L)	5.5	4.5	5.9	4.5
Silver (ug/L)	< 0.16	< 0.16	< 0.16	< 0.16
Thallium (ug/L)	0.27	0.36	0.28	0.31
Zinc (ug/L)	8.1	9.1	5.5	6.6

Table 2 – Split Sample Comparison (Inline Process Monitoring Samples vs. Glover Samples)

Constituent	Glover Sample	GAI Inline Process Monitoring Sample	Glover Sample	GAI Inline Process Monitoring Sample	Glover Sample	GAI Inline Process Monitoring Sample
	System Effluent 010 - 6/6 13:57	160606-1357-BET	System Effluent 011 - 6/6 15:06	160606-1506-BET	Effluent 012 - 6/13 09:33	160613-933-AET
Arsenic	2.0	2.1	1.8	2.2	1.3	1.6
Copper	< 1.0	< 0.56	< 1.0	< 0.56	< 1.0	< 0.56
Lead	< 0.50	< 0.21	< 0.50	< 0.21	< 0.50	< 0.21
Nickel	1.7	1.6	1.7	1.7	1.7	1.6
Selenium	3.0	4.3	3.2	3.9	3.6	4.4
Thallium	0.35	0.28	0.34	0.28	0.77	0.73
TSS	< 1.0	-	< 1.0	-	< 1.0	-

Table 3 – Reanalysis of 6/13/16 Compliance Sample

Constituent	6/13 Compliance Sample Compliance Lab	6/13 Compliance Sample Onsite Mobile Lab – Machine A	6/13 Compliance Sample Onsite Mobile Lab – Machine B
Antimony (ug/L)	< QL	1.7	2.1
Arsenic (ug/L)	< QL	1.8	1.5
Cadmium (ug/L)	< QL	< 0.040	< 0.040
Chromium (ug/L)	< QL	< 0.86	1.7
Copper (ug/L)	< QL	0.85	2.7
Lead (ug/L)	< QL	0.24	0.37
Mercury (ug/L)	< QL	< 0.048	< 0.048
Nickel (ug/L)	< QL	1.1	1.8
Selenium (ug/L)	< QL	3.9	4.2
Silver (ug/L)	< QL	< 0.16	< 0.16
Thallium (ug/L)	0.82	0.57	0.64
Zinc (ug/L)	38.4	29	43

Table 4 – Reanalysis of 6/15/16 Compliance Sample

Constituent	6/15 Compliance Sample Compliance Lab	6/15 Compliance Sample Onsite Mobile Lab – Machine A	6/15 Compliance Sample Onsite Mobile Lab – Machine B
Antimony (ug/L)	< QL	2.5	2.5
Arsenic (ug/L)	< QL	1.7	1.4
Cadmium (ug/L)	< QL	< 0.040	< 0.040
Chromium (ug/L)	< QL	< 0.86	2.3
Copper (ug/L)	< QL	1.7	2.3
Lead (ug/L)	< QL	0.55	0.57
Mercury (ug/L)	< QL	< 0.048	< 0.048
Nickel (ug/L)	< QL	2.3	2.5
Selenium (ug/L)	< QL	4.8	4.7
Silver (ug/L)	< QL	< 0.16	< 0.16
Thallium (ug/L)	0.62	0.47	0.49
Zinc (ug/L)	98.4	87	110

Summary of Split Sample Statistical Analyses

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GAI Project Number C150132.00, Task 065

Statistical analyses were prepared using split sample data collected on 6/20, 6/21, 6/23, 6/24, and 6/25. Data sets were compared by preparing linear regressions and evaluating the strength of correlation between the two sets of data. Strength of correlation is represented by an R^2 value, with a perfect correlation corresponding to an R^2 value of 1.0. The closer the R^2 value is to 1.0, the stronger the correlation.

ZINC: Comparison of Lab Results (Offsite vs. Onsite Mobile Lab and Undigested vs. Digested Samples)

Correlation data obtained by comparing corresponding sets of zinc lab results are shown in Tables 1 and 2. Table 1 summarizes the observed correlation obtained using all available raw data. Table 2 summarizes the observed correlation following removal of potential outlier values. Outliers were defined as all data values that demonstrated a relative percent difference between mobile and offsite lab results greater than or equal to 80%. In total, four outlier values were removed from the analyses summarized in Table 2.

Both statistical analyses performed using split sample zinc data demonstrated very strong correlations between mobile and offsite lab data for both digested and undigested samples. All observed zinc correlations had an R^2 value greater than 0.91, indicating a very strong correlation between offsite and onsite lab data. Removal of outlier values improved the observed correlation slightly.

A strong correlation was also observed between digested and undigested offsite sample results for zinc. These results indicate that the digestion step of the analytical procedure does not produce a large variation in sample results when compared to undigested results.

Table 1: Summary of Statistical Analysis Results for Zinc (All Raw Data)

Sample Comparison	R^2
Offsite Lab Undigested vs. Offsite Digested	0.9295
Offsite Digested vs. Mobile Lab	0.9909
Offsite Undigested vs. Mobile Lab	0.9110

Table 2: Summary of Statistical Analysis Results for Zinc (Potential Outliers Removed)

Sample Comparison	R^2
Offsite Lab Undigested vs. Offsite Digested	0.9936
Offsite Digested vs. Mobile Lab	0.9904
Offsite Undigested vs. Mobile Lab	0.9792

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SELENIUM: Comparison of Lab Results (Offsite vs. Onsite Mobile Lab and Undigested vs. Digested Samples)

Correlation data obtained by comparing corresponding sets of selenium lab results are shown in Table 3. A strong correlation was observed between digested and undigested offsite sample results for selenium. These results indicate that the digestion step of the analytical procedure does not produce a large variation in sample results when compared to undigested results.

Correlations between offsite lab and onsite mobile lab selenium concentrations were somewhat weaker than those observed for zinc. However, the observed relative percent difference between mobile and offsite lab measurements indicated that the current Column C threshold value that is being employed for selenium (6.8 ug/L) provides a sufficient degree of contingency to account for variation between the two labs. For a majority of the samples that were analyzed, the difference between selenium concentrations measured at the mobile and offsite labs was less than 1 ppb.

Table 3: Summary of Statistical Analysis Results for Selenium

Sample Comparison	R^2
Offsite Lab Undigested vs. Offsite Digested	0.9478
Offsite Digested vs. Mobile Lab	0.7683
Offsite Undigested vs. Mobile Lab	0.6129

ARSENIC: Comparison of Lab Results (Offsite vs. Onsite Mobile Lab and Undigested vs. Digested Samples)

Correlation data obtained by comparing corresponding sets of arsenic lab results are shown in Table 4. In total, one outlier value was removed from the analyses summarized in Table 4.

Statistical analyses performed using split sample arsenic data demonstrated very strong correlations between mobile and offsite lab data for both digested and undigested samples. All observed arsenic correlations had an R^2 value greater than 0.97, indicating a very strong correlation between offsite and onsite lab data.

A very strong correlation was also observed between digested and undigested offsite sample results for arsenic. These results indicate that the digestion step of the analytical procedure does not produce a large variation in sample results when compared to undigested results.

Table 4: Summary of Statistical Analysis Results for Arsenic (One Potential Outlier Removed)

Sample Comparison	R^2
Offsite Lab Undigested vs. Offsite Digested	0.9937
Offsite Digested vs. Mobile Lab	0.9882
Offsite Undigested vs. Mobile Lab	0.9736

COPPER: Comparison of Lab Results (Offsite vs. Onsite Mobile Lab and Undigested vs. Digested Samples)

Correlation data obtained by comparing corresponding sets of copper lab results are shown in Table 5. In total, one outlier value was removed from the analyses summarized in Table 5.

Statistical analyses performed using split sample copper data demonstrated very strong correlations between mobile and offsite lab data for both digested and undigested samples. All observed copper correlations had an R^2 value greater than 0.93, indicating a very strong correlation between offsite and onsite lab data.

A strong correlation was also observed between digested and undigested offsite sample results for copper. These results indicate that the digestion step of the analytical procedure does not produce a large variation in sample results when compared to undigested results.

Table 5: Summary of Statistical Analysis Results for Copper (One Potential Outlier Removed)

Sample Comparison	R^2
Offsite Lab Undigested vs. Offsite Digested	0.9328
Offsite Digested vs. Mobile Lab	0.9401
Offsite Undigested vs. Mobile Lab	0.9325

NICKEL: Comparison of Lab Results (Offsite vs. Onsite Mobile Lab and Undigested vs. Digested Samples)

Correlation data obtained by comparing corresponding sets of nickel lab results are shown in Table 6. Table 6 summarizes the observed correlation obtained using all available raw data.

One statistical analysis performed using split sample nickel data demonstrated a very strong correlation between mobile and offsite lab data for digested samples. The observed nickel correlation had an R^2 value greater than 0.91, indicating a strong correlation between offsite and onsite lab data for digested samples. However, there was a weaker correlation between offsite undigested vs. mobile data with an R^2 value at 0.7058.

A relatively weak correlation was also observed between digested and undigested offsite sample results for nickel. These results indicate that the digestion step of the analytical procedure may produce a large variation in sample results when compared to undigested results. For 18/23 data pairs, the undigested sample demonstrated a higher concentration of nickel than the digested sample.

Table 6: Summary of Statistical Analysis Results for Nickel (One Potential Outlier Removed)

Sample Comparison	R^2
Offsite Lab Undigested vs. Offsite Digested	0.7401
Offsite Digested vs. Mobile Lab	0.9164
Offsite Undigested vs. Mobile Lab	0.7058

ADDITIONAL METALS: Antimony, Cadmium, Chromium, Lead, Mercury, Silver, and Thallium

Split sample data for cadmium, chromium, lead, mercury, silver, and thallium were insufficient for development of linear regression models. For each of these metals, not enough sample pairs contained constituent concentrations above the laboratory limit of detection for statistical analysis. GAI will continue to collect split samples periodically as treatment progresses, and analysis of these metals will be revisited as more data is collected.

Split sample data for antimony did not demonstrate a wide enough range of measureable concentrations for development of a linear regression model. Antimony measurements for both the mobile and offsite labs were very consistent, and none of the samples (including treatment system influent samples) demonstrated an antimony concentration > 4 ppb. All constituent concentrations were < 0.5% of the Monthly Average Effluent Limitation for antimony (1,300 ppb).

Comparison of Pace Offsite Lab Results vs. Independent Third Party Lab Results

Split samples collected on 6/23 were analyzed by the onsite mobile lab, the Pace offsite compliance lab, and an additional independent third party lab. Sample results for the Pace offsite lab and the independent third party lab were compared to ensure that the Pace offsite lab data is directly comparable to data produced by other labs that may potentially be used for compliance sample analysis. Linear regressions were prepared using offsite lab data for five metals: arsenic, copper, nickel, selenium, and zinc. Correlation data obtained by comparing corresponding sets of data results from the two offsite labs are shown in Tables 7 and 8. Table 7 contains correlations for undigested sample results, while Table 8 contains correlations for digested sample results.

Table 7: Summary of Correlation data for Comparison of Pace Offsite Compliance Lab Data vs. Data from an Independent Third Party Lab (Undigested Samples)

Constituent	R^2
Arsenic	0.9932
Copper	0.9346
Nickel	0.8914
Selenium	0.9685
Zinc	0.9939

Table 8: Summary of Correlation data for Comparison of Pace Offsite Compliance Lab Data vs. Data from an Independent Third Party Lab (Digested Samples)

Constituent	R^2
Arsenic	0.9982
Copper	0.9181
Nickel	0.9586
Selenium	0.9890
Zinc	0.9702

Strong correlations were observed between data sets for each of the five constituents that were evaluated for both digested and undigested samples. These data verify that the compliance lab results are strongly correlated with results produced by a similar independent lab.

Sample Comparison: Compliance Sample Results vs. Internal Process Sampling Results

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Compliance sample data was compared with Internal Process sampling results for each Compliance sample that has been collected to date. To perform this comparison, the average observed constituent concentrations were calculated for all Internal Process sampling results collected within four hours prior to collection of Compliance samples. The average value of the Internal Process sampling results was used for comparison since this value provides an approximation of the water quality in the temporary storage tank whenever Compliance samples are collected. Results of this comparison for each constituent are summarized below.

SELENIUM

For 8/18 Compliance samples that have been collected to date, average Internal Process sampling results from the mobile lab demonstrated concentrations at or below the Quantification Limit (QL) for selenium used by the Compliance lab (5.0 ppb). All corresponding Compliance sampling data for these days were reported as <QL. Based on these results, there was no quantifiable difference between Compliance and Internal Process sampling data for selenium on these sampling days.

All data for Compliance sampling days when Internal Process sampling data differed slightly from Compliance sampling results are shown in Table 1. The difference between Internal Process sampling and Compliance sampling results ranged from 0.1 – 1.7 ppb, with an average difference of 0.4 ppb. For a majority of sample pairs, Internal Process sampling results were slightly higher than Compliance sampling results. With the exception of one sampling date, all Compliance sampling results were within 10% of the corresponding Internal Process sampling results.

Table 1: Compliance vs. Internal Process Sampling Results (Selenium)

Sample Date & Time	Average Internal Process Sampling Result (ppb)	Compliance Lab Result (ppb)	Δ (Mobile - Compliance) (ppb)	% Difference
6/8/2016, 15:26	5.2	< 5.0	0.2	+4%
6/13/2016, 17:45	5.4	< 5.0	0.4	+8%
6/15/2016, 17:46	5.4	< 5.0	0.4	+8%
6/23/2016, 18:35	5.2	< 5.0	0.2	+4%
6/25/2016, 18:36	5.9	5.7	0.2	+4%
6/28/2016, 12:00	6.0	6.3	-0.3	-5%
6/30/2016, 20:33	6.0	6.5	-0.5	-8%
7/11/2016, 11:10	6.2	6.1	0.1	+2%
7/13/2016, 18:07	6.2	6.0	0.2	+3%
7/29/2016, 16:20	6.7	< 5.0	1.7	+34%

THALLIUM

For 16/18 Compliance samples that have been collected to date, average Internal Process sampling results from the mobile lab demonstrated concentrations at or below the QL for thallium used by the Compliance lab (0.47 ppb). All corresponding Compliance sampling data for these days were reported as <QL. Based on these results, there was no quantifiable difference between Compliance and Internal Process sampling data for thallium on these sampling days.

All data for Compliance sampling days when Internal Process sampling data differed slightly from Compliance sampling results are shown in Table 2. The difference between Internal Process sampling and Compliance sampling results ranged from 0.14 – 0.17 ppb, with an average difference of 0.16 ppb. For each of the two sample pairs that showed differences between Internal Process sampling and Compliance sampling results, thallium concentrations were slightly lower in Internal Process samples than Compliance samples. The observed percent differences between the two sets of results were both below 25%.

Table 2: Compliance vs. Internal Process Sampling Results (Thallium)

Sample Date & Time	Average Internal Process Sampling Result (ppb)	Compliance Lab Result (ppb)	Δ (Mobile - Compliance) (ppb)	% Difference
6/13/2016, 17:45	0.65	0.82	-0.17	-21%
6/15/2016, 17:46	0.48	0.62	-0.14	-23%

ZINC

On 15/18 Compliance sampling days, average Internal Process sampling results from the mobile lab demonstrated concentrations at or below the QL for zinc used by the Compliance lab (25 ppb). All corresponding Compliance sampling data for these days was reported as <QL. There was no quantifiable difference between Compliance and Internal Process sampling data for zinc on these sampling days.

All data for Compliance sampling days when Internal Process sampling data differed slightly from Compliance sampling results are shown in Table 3.

Table 3: Compliance vs. Internal Process Sampling Results (Zinc)

Sample Date & Time	Average Internal Process Sampling Result (ppb)	Compliance Lab Result (ppb)	Δ (Mobile - Compliance) (ppb)	% Difference
6/10/2016, 15:28	2.4	26.0	-23.6	-91%
6/13/2016, 17:45	10.2	38.4	-28.2	-73%
6/15/2016, 17:46	10.3	98.4	-88.1	-90%

The difference between Internal Process sampling and Compliance sampling results ranged from 23.6 – 88.1 ppb, with an average difference of 46.7 ppb. Following observation of these differences, extra Compliance sample water that was collected on two of these three sampling days (6/13 and 6/15) was reanalyzed by the mobile lab. This reanalysis was performed on each of the two ICP-MS machines that are used by the mobile lab (Machines A and B), and the results of these reanalyses are shown in Tables 4 and 5.

Table 4: Compliance vs. Mobile Lab Reanalysis Results (Zinc) – Machine A

Sample Date & Time	Mobile Lab Reanalysis Result – Machine A (ppb)	Compliance Lab Result (ppb)	Δ (Mobile Machine A - Compliance) (ppb)	Machine A % Difference
6/13/2016, 17:45	29	38.4	-9.4	-24%
6/15/2016, 17:46	87	98.4	-11.4	-12%

Table 5: Compliance vs. Mobile Lab Reanalysis Results (Zinc) – Machine B

Sample Date & Time	Mobile Lab Reanalysis Result – Machine B (ppb)	Compliance Lab Result (ppb)	Δ (Mobile Machine B - Compliance) (ppb)	Machine B % Difference
6/13/2016, 17:45	43	38.4	4.6	12%
6/15/2016, 17:46	110	98.4	11.6	12%

Zinc concentrations observed upon reanalysis of the Compliance samples by the mobile lab were much closer to results reported by the Compliance sampling lab. These results indicated that a source of zinc contamination may be contributing to the disparity observed between Internal Process and Compliance sampling results. Based on this observation, a survey of the treatment system was performed to identify any potential sources of zinc contamination between the Internal Process sampling port and the Compliance sampling point. Several brass fittings were identified between the two sampling locations, and these fittings were subsequently replaced with stainless steel fittings to prevent potential leaching of zinc. Following replacement of these fittings, all Internal Process samples and Compliance samples have demonstrated zinc concentrations < 25 ppb.

ADDITIONAL CONSTITUENTS

To date, all measurements for Compliance samples have been reported by the Compliance lab as below the Quantification Limit specified by the VPDES permit (< QL) for the following constituents:

- Antimony
- Arsenic
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Silver

All corresponding Internal Process Monitoring data from the mobile lab for these constituents have demonstrated concentrations below the QL as well. As a result, no quantifiable differences have been observed between Compliance and Internal Process Monitoring sample results for these constituents.

Mobile Lab Split Sample Comparison: ICP-MS Machine A vs. Machine B

Possum Point CCB Pond Closure Project

GAI Project Number C150132.00, Task 065

Several split samples have been collected to date as part of routine Internal Process sampling in an effort to compare the operation of ICP-MS Machines A and B. Split sample collection will be performed on a weekly basis as the project continues, and each sample will be evaluated on each of the two machines. A summary of all Internal Process split sample results is provided below. This summary includes results for Internal Process split samples collected between 6/19 and 6/22.

Internal Process split sample summarized in Table 1 below were generated from 20 split sample events collected from 6/19 to 6/22.

Table 1: Internal Process Split Sample Results

Constituent	Machine A Average Concentration (ppb)	Machine B Average Concentration (ppb)	Average Observed Δ |A – B| (ppb)	Average Observed % Difference
Antimony	3.4	3.2	0.4	11%
Arsenic	2.2	1.6	0.6	35%
Cadmium	< 0.040	< 0.040	0.000	0%
Chromium	< 0.86	0.62	0.23	14%
Copper	< 0.56	< 0.56	0.00	0%
Lead	< 0.21	< 0.21	0.00	0%
Mercury	< 0.048	< 0.048	0.000	0%
Nickel	1.9	2.0	0.3	15%
Selenium	6.2	5.3	1.3	21%
Silver	< 0.16	< 0.16	0.00	0%
Thallium	0.25	0.29	0.05	17%
Zinc	7.0	8.7	2.0	25%

NO VARIABILITY

The following constituents have demonstrated no quantifiable differences when measured using Machine A or B:

- Cadmium
- Copper
- Lead
- Mercury
- Silver

LOW TO MODERATE VARIABILITY (<20%)

Constituents with measurements on Machines A and B that were within 20% of one another included the following:

- Antimony
- Chromium
- Nickel
- Thallium

This 20% range is within the expected range of variability for analysis of the same water sample on different analytical machines.

HIGH VARIABILITY (>20%)

Constituents with measurements on Machines A and B that differed by >20% included the following:

- Arsenic
- Selenium
- Zinc

Arsenic demonstrated the highest observed percent difference (35%) between constituent concentrations measured on Machines A and B. However, the average difference between arsenic measurements was only 0.6 ppb. This difference represents 0.25% of the effluent limitation specified by the Station's VPDES permit. Average observed arsenic concentrations for each machine were <1% of the effluent limitation for Internal Outfall 503. The high observed percent difference between arsenic measurements may be explained by the fact that the observed arsenic concentrations in Internal Process samples have been very low and during this test period eighteen of the results produced by the instruments were qualified with "The analyte was detected but is below the reporting limit. The concentration is estimated." Since arsenic is being detected at levels at the limit of detection or approaching the limit of detection for the ICP-MS, this level of variability is not unusual.

Selenium measurements produced by the two machines differed by an average of 21%. Like arsenic, selenium concentrations observed in the Inline Process samples have been approaching the ICP-MS limit of detection. As a result, greater variability may be expected when analyzing concentrations that are close to the machine's detection limit. The average observed concentrations indicate that Machine A consistently reads higher than Machine B by approximately 1.3 ppb. That said, during this test period eight of the results produced by Machine A were qualified with "Results might be biased high because of continuing calibration verification (CCV)." Pace has expressed that the fact that each ICP-MS has individual argon units each with varying levels of krypton gas contamination and this will affect selenium results, especially as the observed concentrations are approaching the ICP-MS limit of detection.

Zinc measurements produced by the two machines differed by an average of 25%. The average observed concentrations for each of the two machines were <10% of the effluent limitations specified by the VPDES permit. During this test period, eighteen of the results produced by the instruments were qualified with as potentially biased high or low. Like arsenic and selenium, the variability observed between the two machines may be due to the fact that the observed concentrations are approaching the ICP-MS limit of detection.

MEMORANDUM

Date	August 9, 2016
Subject	Proposed Method Modifications – Pace On-Site Laboratory
To	GAI Consultants
From	Nick Nigro

This memorandum addresses two proposed enhancements to the Pace On-Site Laboratory Standard Operating Procedure (SOP) to address (a) two-system operation and optimization, and (b) optimizing the existing method to better evaluate selenium precision and accuracy.

Two System Operation and Optimization

Given the required objective to eliminate to the extent practical a sample result turnaround time of greater than 1 hour, Pace proposes that the two on-site instruments be used in the following manner over a 24-hour time period:

1. **Instrument A** (middle room) will be used for analysis from 1900 to 0700 hours. Instrument tuning and calibration will take place at the end of the previous shift starting at ~1700.
2. **Instrument B** (small room) will be used for analysis from 0700 to 1900 hours. Instrument tuning and calibration will take place at the end of the previous shift starting at ~0500.

Pace will continue to qualify results as per the standard method protocols. Pace will increase the frequency of QC checks and will add a 5 ppb LCV, LCV3, (for selenium) as described below. The 5 ppb LCV standard for selenium will be closely monitored, and if it is low or high the exact recovery percentage will be communicated to GAI. Depending on the analytical result (and associated LCV recovery) relative to the project action limit(s), GAI may choose to continue analysis if deemed "marginal" and if deemed not to affect decision making ability. For example, a selenium result of 8 ppb that is qualified with a low LCV recovery of 68% may in fact be deemed to be suitable for decision making purposes and thus continued instrument operation.

If the exceedance(s) is found to be outside of the marginal exceedance limits (to be set by GAI), or whenever required by GAI, the primary instrument will be recalibrated if time allows, or the second instrument will have a CCV, LCV(s) and CCB suite of standards analyzed and analysis will be moved to that instrument.

This two-system operation is the optimal approach but will be adjusted as needed when one of the following occurs: (a) either instrument needs routine PM requiring it to be "down" for a short period of time, (b) either instrument needs to be recalibrated (which may be needed for multiple reasons), or (c) either instrument becomes unsuitable for operation (i.e., not a critical failure but one that requires a longer evaluation period than what routine PM would involve). Pace will be most diligent to ensure two-system operation during 24-hour compliance testing events.

Increasing Selenium QC

Currently, a CCV, LCV(s) and CCB set of standards are analyzed every 10 samples or every 4 hours, whichever is more frequent. Pace will add a 5 ppb LCV standard, LCV3, (for selenium) to each sample batch submission. With an LCV being analyzed with every sample delivery batch, and having it set at the 5 ppb selenium reporting limit, it should be easier to monitor analyte drift that may be occurring on the instrument being used. If there is an exceedance of the allowable recovery limits for that 5 ppb selenium LCV (currently set at ±30%), the analyst will qualify the selenium data and will also write the selenium recovery of the hourly LCV standard next to the sample results that are associated with the failing LCV standard. See also previous discussion on instrument corrective action protocols that will be followed in these instances.